



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 003 701 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
27.11.2002 Bulletin 2002/48

(51) Int Cl.7: **C07C 29/84, C07C 29/80,
C07C 31/04, C07C 47/09**

(21) Application number: **98939642.9**

(86) International application number:
PCT/EP98/04695

(22) Date of filing: **27.07.1998**

(87) International publication number:
WO 99/008985 (25.02.1999 Gazette 1999/08)

(54) **PURIFICATION OF A METHANOL STREAM**
REINIGUNG VON EINEM METHANOLSTROM
PURIFICATION D'UN FLUX DE METHANOL

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(74) Representative: **De Hoop, Eric, Drs. et al**
Octroolbureau Vriesendorp & Gaade,
Dr Kuiperstraat 6
2514 BB Den Haag (NL)

(30) Priority: **15.08.1997 US 911972**

(43) Date of publication of application:
31.05.2000 Bulletin 2000/22

(56) References cited:
GB-A- 893 730 US-A- 4 388 154

(73) Proprietor: **ARCO Chemical Technology, L.P.**
Greenville, Delaware 19807 (US)

(72) Inventors:
• **RUETER, Michael, A.**
Norristown, PA 19401 (US)
• **JUBIN, John, C., Jr.**
West Chester, PA 19382 (US)

• **CHEMICAL ABSTRACTS, vol. 88, no. 25, 19 June 1978 Columbus, Ohio, US; abstract no. 190069s, page 697; XP002082578 & JP 53 001246 B (TOYO CHEMICAL INDUSTRY, ET AL.) 17 January 1978**
• **M.G. CLERICI, ET AL.: "Synthesis of propylene oxide from propylene and hydrogen peroxide catalysed by titanium silicalite" JOURNAL OF CATALYSIS, vol. 129, no. 1, 1 May 1991, pages 159-167, XP000577042 Duluth, US cited in the application**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 003 701 B1

Description**FIELD OF THE INVENTION**

5 **[0001]** This invention pertains to the purification of a methanol stream contaminated with acetaldehyde. In particular, the invention relates to an extractive distillation method wherein a polar substance such as water or propylene glycol is used to enhance the volatility of acetaldehyde relative to methanol, enabling the acetaldehyde impurities to be more easily separated as an overhead stream from the methanol.

10 **BACKGROUND OF THE INVENTION**

[0002] In recent years, the production of propylene oxide from propylene using hydrogen peroxide as an oxidant and a titanium-containing zeolite as a catalyst has been proposed. Methanol is a particularly preferred reaction solvent for such purposes, as it tends to promote high catalyst activity and selectivity. Epoxidation processes of this type are 15 described, for example, in U.S. Pat. Nos. 5,591,875, 4,833,260, 5,621,122, 5,646,314, and 4,824,976, EP Pub. No. 0732327, and Clerici et al., *J. Catalysis* 129, 159-167 (1991), the teachings of which are incorporated herein by reference in their entirety. Although such processes are capable of providing exceptionally high selectivity to propylene oxide, minor quantities of certain by-products such as acetaldehyde are inevitably formed.

[0003] The methanol which is recovered following the separation of unreacted propylene and propylene oxide from the crude epoxidation reaction product often is contaminated with acetaldehyde. In addition to the acetaldehyde produced during epoxidation, acetaldehyde may be generated during the methanol recovery steps. Normally, it will be economically advantageous to recycle the recovered methanol for use in the epoxidation process. While low concentrations of acetaldehyde generally may be present in the epoxidation reaction mixture without deleterious effect on the epoxidation, in a continuous process the acetaldehyde will tend to accumulate in the methanol recycle stream to an 25 unacceptable level. At high concentrations, for example, the accumulated acetaldehyde can contaminate the propylene oxide being produced. The complete separation of acetaldehyde from propylene oxide is difficult, however. It will thus be highly desirable to develop a means by which at least a portion of the acetaldehyde may be effectively separated from the recovered methanol prior to the methanol being reintroduced to the epoxidation reactor.

30 **SUMMARY OF THE INVENTION**

[0004] This invention provides a method of removing acetaldehyde from an impure methanol stream comprising (a) introducing the impure methanol stream into an intermediate section of an extractive distillation zone, (b) introducing an extractive solvent stream comprised of a polar substance selected from the group consisting of water, glycols, glycol 35 ethers and mixtures thereof to an upper section of said extractive distillation zone, (c) distilling acetaldehyde overhead from said extractive distillation zone, and (d) recovering from a lower section of said extractive distillation zone a bottoms stream comprising methanol and the polar substance and having a reduced acetaldehyde concentration as compared to the impure methanol stream.

[0005] The bottoms stream may thereafter be introduced into an intermediate section of a fractional distillation zone, the methanol distilled overhead from said fractional distillation zone, and a second bottoms stream comprising the polar substance recovered from a lower section of said fractional distillation zone.

[0006] In another embodiment of the invention, only a portion of the impure methanol stream is fed to the extractive distillation zone with the remaining portion being fed directly to the fractional distillation zone in the same manner as the bottoms stream from the extractive distillation zone.

45 **[0007]** In yet another embodiment of the invention, the impure methanol stream is additionally comprised of at least one polar substance other than water, and the second bottoms stream is subjected to an additional fractional distillation to remove water overhead and to obtain a third bottoms stream comprised of the polar substance which is recycled for use as the extractive solvent stream in step (c).

50 **DESCRIPTION OF THE DRAWING**

[0008] Figure 1, to be explained in more detail hereafter, illustrates in schematic form an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

55 **[0009]** The impure methanol stream treated in accordance with the process of this invention is typically obtained by subjecting a crude epoxidation reaction product containing methanol as a solvent to an initial fractionation or series of fractionations wherein most or all of the unreacted propylene and the propylene oxide product are first removed by

means of distillation or the like. The crude epoxidation reaction product may be generated by reacting propylene and hydrogen peroxide in a liquid phase comprised of methanol in the presence of a catalytically effective amount of a titanium-containing zeolite such as titanium silicalite (TS-1), as described in the references listed in the Background section of this application. Depending upon the epoxidation conditions and initial fractionation means employed, the impure methanol stream generally will have a composition comprised of the following components, in percent by weight:

Methanol	60 to 90
Acetaldehyde	0.01 to 0.1
Water	5 to 40
Glycols, glycol ethers, other heavy impurities	0.1 to 2

[0010] Other components may, of course, also be present such as propylene, propylene oxide and reaction by-products and other impurities; typically, however, methanol will comprise at least 60 weight percent of the impure methanol stream. Any water or other polar substance present in the feed is taken into consideration in the calculation of the amount of polar substance to be supplied to the extractive distillation. Whatever the content of polar substance in the feed, however, the amount of polar substance supplied in a separate extractive solvent stream preferably may be at least about 25% by weight, based on the weight of the impure methanol stream. The amount of polar substance introduced into the extractive distillation zone is preferably 40 to 60 weight percent of the impure methanol stream feed.

[0011] The extractive distillation is suitably carried out in any convenient distillation column or tower appropriate for the distillation of methanol. The column or tower is equipped with an appropriate reflux condensing means and an appropriate reboiler heating means. For best results, the extractive distillation zone should contain at least 10 theoretical plates and ordinarily will contain 20 to 30 theoretical plates. The maximum number of theoretical plates is limited only by economic considerations. A single distillation column or tower is usually preferred for economic reasons, but the use of multiple distillation columns to accomplish the same result is not excluded.

[0012] The extractive solvent stream supplied to the extractive distillation zone will be comprised predominantly (e.g., at least 90 percent by weight) of one or more polar substances having volatilities less than that of methanol. Suitable polar substances for purposes of this invention include, water, glycols, glycol ethers and mixtures thereof. The term "glycols" refers to dihydric alcohols such as, for example, ethylene glycol, 1,2-propylene glycol, 1,3-propane diol, 1,4-butanediol, neopentyl glycol, 2-methyl 1,3-propanediol, 1,3-butanediol, 2,3-butanediol and the like and oligomers thereof such as diethylene glycol, tripropylene glycol, and the like. The term "glycol ethers" refers to mono- and diethers of glycols, and glycol oligomers, with mono-alkyl ethers generally being preferred (e.g., propylene glycol monomethyl ether). It is preferred that the polar substance or mixture of polar substances selected comprise at least 85 weight percent, more preferably at least 95 weight percent of the extractive solvent stream. The feed point for the extractive solvent stream should be between the impure methanol stream feed point and the point at which the overhead stream comprising acetaldehyde is withdrawn from the extractive distillation zone. This will help to prevent contamination of the overhead stream by the extractive solvent stream, if so desired. Preferably, the extractive solvent stream is introduced to the extractive distillation zone at a point not less than 1 theoretical plate below the overhead stream withdrawal point and not less than 5 theoretical plates above the point where the impure methanol stream is introduced. Some methanol may be withdrawn overhead together with acetaldehyde; while it will generally be desirable to minimize the amount of overhead methanol, one of the advantages of this invention is that such losses typically represent only a small fraction (e.g., 1% or less) of the total amount of methanol in the impure methanol stream.

[0013] The point at which the impure methanol stream is introduced is an intermediate section of the extractive distillation zone, preferably from about 20% to 50% of the distance, in terms of theoretical plates, from the bottom to the top of the extractive distillation zone.

[0014] A suitable reflux/impure methanol stream feed ratio is important in achieving optimum results and generally will be in the range of from 0.5:1 to 1:1. The pressure under which the extractive distillation is suitably around atmospheric pressure, e.g., from 55 kPa to 345 kPa (about 8 up to about 50 psia) (as measured at the top of the extractive distillation zone). The bottoms (reboiler) temperature will, of course, vary with the pressure but will typically be within the range of 90°C to 120°C.

[0015] The extractive distillation conditions are selected so as to provide, at a minimum, a bottoms stream having a reduced acetaldehyde level as compared to the initial impure methanol stream. While the process of this invention is capable of being operated to remove all or substantially all (i.e., 99+%) of the initially present acetaldehyde, the conditions may also be readily adjusted if so desired so as to achieve a lower degree of acetaldehyde removal (e.g., 50 to 75%).

[0016] Where the initial impure methanol stream contains water in addition to methanol and it is desired to use an extractive solvent stream containing a polar substance or mixture of polar substances which is less volatile than water (although some water may be present as a mixture with the other polar substances) and to remove at least a portion

of the water from the system so as to maintain a certain concentration of water in the extractive solvent stream, the following embodiment of the invention may be practiced. The bottoms product withdrawn from the fractional distillation zone is fed to an intermediate section of a second fractional distillation zone and fractionally distilled under conditions effective to take the desired amount of water overhead and to yield a third bottoms stream comprised of the polar substance which is withdrawn from a bottom section of the second fractional distillation zone. This third bottoms stream may then be recycled for use as the extractive solvent stream.

[0017] Another desirable embodiment of the present process is to feed only a portion (e.g., 5 to 30 percent by weight) of the impure methanol stream to the extractive distillation zone. The remainder is bypassed directly to the first fractional distillation zone, preferably being introduced to an intermediate section in the same manner as the first bottoms stream.

The second portion of the impure methanol stream and the first bottoms stream may be fed separately or, if so desired, first combined prior to introducing into the first fractional distillation zone. This accomplishes the desired removal of a portion of the acetaldehyde from the impure methanol stream, but significantly reduces the energy and equipment costs of the process due to ability to utilize a smaller capacity extractive distillation zone than would be needed to handle the entire impure methanol stream.

[0018] In the accompanying drawing (Figure 1) there is illustrated diagrammatically a representative system for carrying out the extractive distillation process of this invention. Thus, referring to the drawing, the reference numeral 1 designates the line for feeding a portion of the impure methanol stream to be treated to an extractive distillation zone 2. Heat may be supplied to the column or tower comprising the extractive distillation zone by means of a reboiler. Water is supplied as the extractive distillation solvent through line 3 in the form of an aqueous stream. The aqueous stream may additionally contain water-soluble organic substances such as glycols, glycol ethers and the like. The bottoms stream comprising methanol and water, but with a reduced acetaldehyde concentration, is withdrawn through line 4. The acetaldehyde is removed in vapor form as an overhead stream via line 5 and thereafter condensed and recovered for chemical value, burned as fuel, or sent to waste disposal. The bottoms stream is fed into an intermediate section of fractionator 6, which may be a conventional fractional distillation column or tower of appropriate materials and capacity, and subjected to fractional distillation. The remaining portion of the impure methanol stream supplied to the purification section described herein via line 10 is also fed into an intermediate section of fractionator 6 by way of line 11. Methanol in purified form is taken overhead via line 7 and may be recycled for use as a reaction solvent in an olefin epoxidation process. A bottoms stream comprised of water, which will generally also contain compounds less volatile under the distillation conditions than methanol, is withdrawn from a lower section of fractionator 6 through line 8. A portion of this bottoms stream may be returned by means of line 3 for further use as the extractive distillation stream in the extractive distillation step of the process. The remaining portion of the bottoms stream is withdrawn through line 9 for disposal. The amount of the bottoms stream removed in this manner may advantageously be adjusted to compensate for the amount of water generated from hydrogen peroxide as a co-product in the olefin epoxidation process.

Example

[0019] This example demonstrates the purification of an impure methanol stream in accordance with the present invention. The impure methanol stream has the following composition:

Component	Wt. %
Methanol	80.5
Water	18.3
Acetaldehyde	0.044
Propylene Glycol	0.23
Other Heavy Components	0.926

[0020] Of 100 parts by weight of this methanol stream, 13.3 parts are fed to a first distillation column (where extractive distillation is performed) while 86.7 parts are bypassed to a second tower (where fractional distillation is performed).

[0021] The first distillation tower contains 25 theoretical stages, including the reboiler. The impure methanol stream (13.3 parts) is fed to the 18th stage from the top and 6.8 parts by weight of water containing low levels of various organic impurities are fed to the second stage from the top. An overhead stream containing acetaldehyde is withdrawn from the top stage and condensed in a total condenser. The bulk of the methanol and water is withdrawn from the bottom stage (reboiler) and fed forward to the second tower. The first tower is operated at a reflux ratio (reflux to impure methanol feed) of 0.8. The pressure in the column condenser is set at 262 kPa (38 psia) and the column operated with a pressure drop of 2.8 kPa (0.4 psi) per tray such that the bottom pressure is approximately 345 kPa (50 psia). This results in a bottoms (reboiler) temperature of 112°C and a top (condenser) temperature of 91°C.

[0022] Under these conditions, 75% of the acetaldehyde in the impure methanol stream fed to the first tower is recovered in the overhead distillate product. This represents 10% of the acetaldehyde in the total impure methanol stream. Of the amounts in the first tower feed, only 0.16% of the methanol and 0.23% of the water are taken overhead with the acetaldehyde. The compositions of the two streams obtained from the first tower are as follows:

Component	Distillate (wt.%)	Bottoms(wt.%)
Methanol	58.3	53.5
Water	18.2	42.8
Acetaldehyde	14.6	0.0073
Propylene Glycol	0	0.73
Other Heavy Components .	0	2.96

[0023] The bottoms stream from the first tower (20 parts by weight) is fed to the second distillation tower together with the 86.7 parts of the initial impure methanol stream which bypasses the first tower.

[0024] The second distillation tower contains 20 theoretical stages (including reboiler). The feed streams are introduced at the 4th stage from the top. An overhead stream of purified methanol (86.8 parts) is withdrawn from the top stage and condensed in a total condenser. The balance of the water and heavy components is withdrawn from the bottom stage (reboiler). Of this bottoms stream, 13.3 parts are fed to the first distillation tower for reuse as the extractive solvent stream and the remainder is removed for disposal as waste.

[0025] The second tower operates at a reflux ratio (reflux to feed) of 0.44. The pressure in the column condenser is 1103 kPa (160 psia) and the column operated with a pressure drop of 3.4 kPa (0.5 psi) per tray such that the bottom pressure is 1172 kPa (170 psia). This results in a bottoms (reboiler) temperature of 187°C and a top (condenser) temperature of 144°C.

[0026] Under the above-described conditions, 99.9% of the methanol in the feed to the second tower is recovered in the overhead distillate stream. The compositions of the two streams withdrawn from the second tower are as follows:

Component	Distillate (wt.%)	Bottoms(wt.%)
Methanol	92.6	0.48
Water	7.25	91.0
Acetaldehyde	0.0046	0
Propylene Glycol	0	1.72
Other Heavy Components,	0	6.8

[0027] The distillate (overhead) stream may be recycled for use as a source of methanol in a propylene epoxidation process of the type described in EP Pub. No. 0732327 (corresponding to U.S. Ser. No. 08/404,657, filed March 15, 1995).

Claims

1. A method of removing acetaldehyde from an impure methanol stream comprising

- (a) introducing the impure methanol stream into an intermediate section of an extractive distillation zone;
- (b) introducing an extractive solvent stream comprised of a polar substance selected from the group consisting of water, glycols, glycol ethers and mixtures thereof into an upper section of said extractive distillation zone;
- (c) distilling acetaldehyde overhead from said extractive distillation zone; and
- (d) recovering from a lower section of said extractive distillation zone a bottoms stream comprising methanol and the polar substance and having a reduced acetaldehyde concentration as compared to the impure methanol stream.

2. The method of claim 1 wherein the amount of the extractive solvent stream introduced into said extractive distillation zone is at least 25 weight percent of the impure methanol stream.

3. The method of claim 1 wherein the polar substance is selected from the group consisting of water, propylene glycol and mixtures thereof

4. The method of claim 1 comprising the additional steps of introducing the bottoms stream into an intermediate section of a fractional distillation zone, distilling methanol overhead from said fractional distillation zone, and recovering a second bottoms stream comprising the polar substance from a lower section of said fractional distillation zone.
5. The method of claim 4 comprising the additional steps of recycling at least a portion of the second bottoms stream to the extractive distillation zone for use as the extractive solvent stream.
6. The method of claim 1 wherein at least 50% of the acetaldehyde in the impure methanol stream is distilled overhead in step (c).
7. The method of claim 1 wherein methanol comprises at least 60 weight percent of the impure methanol stream.
8. A method of removing acetaldehyde from an impure methanol stream according to claim 1 wherein the stream comprises at least 60 weight percent methanol; the extractive solvent stream comprises at least 85 weight percent of a polar substance selected from the group consisting of water, propylene glycol and mixtures thereof; the amount of the extractive solvent stream introduced is at least 25 weight percent of the impure methanol stream and at least 50% of the acetaldehyde in the impure methanol stream is distilled overhead from said extractive distillation zone.
9. The method of claim 8 wherein the impure methanol stream is recovered from an epoxidation process wherein propylene is reacted with hydrogen peroxide using a titanium-containing zeolite as catalyst and methanol as a solvent.
10. The method of claim 8 wherein the impure methanol stream is comprised of 60-80 weight % methanol, 0.01 - 0.1 weight % acetaldehyde, and 5-40 weight % water.
11. The method of claim 8 wherein the amount of the extractive solvent stream is from 40 to 60 weight percent of the impure methanol stream.
12. A method of removing acetaldehyde from an impure methanol stream according to claim 1 comprising
 - (a) introducing a first portion of the impure methanol stream into an intermediate section of an extractive distillation zone; and thereafter
 - (e) introducing the first bottoms stream and a second portion of the impure methanol stream into an intermediate section of a fractional distillation zone;
 - (f) distilling a purified methanol stream overhead from said fractional distillation zone; and
 - (g) recovering from a lower section of the fractional distillation zone a second bottoms stream comprised of the polar substance and having a reduced methanol concentration as compared to the first bottoms stream.
13. The method of claim 12 wherein at least a portion of the second bottoms stream is recycled for use as the extractive solvent stream in step (b).
14. The method of claim 12 wherein the amount of the extractive solvent stream introduced into said extractive distillation zone is at least 25 weight percent of the first portion of the impure methanol stream.
15. The method of claim 12 wherein the first portion of the impure methanol stream is from 5 to 30 percent by weight of the impure methanol stream.
16. The method of claim 12 wherein methanol comprises at least 60 weight percent of the impure methanol stream.
17. The method of claim 12 wherein the polar substance is selected from the group consisting of water, propylene glycol, and mixtures thereof.
18. The method of claim 12 wherein at least 50% of the acetaldehyde in the first portion of the impure methanol stream is distilled overhead in step (c).
19. The method of claim 12 wherein the impure methanol stream is additionally comprised of water, the extractive

solvent stream is comprised of at least one polar substance other than water, and the second bottoms stream is subjected to an additional fractional distillation to remove water overhead and to obtain a third bottoms stream comprised of the polar substance which is recycled for use as the extractive solvent stream in step (c).

- 5 20. The method of claim 12 wherein the polar substance or mixture of polar substances comprises at least 85 weight percent of the extractive solvent stream.

Patentansprüche

10

1. Verfahren zum Entfernen von Acetaldehyd von einem unreinen Methanolstrom umfassend

- 15 (a) Einführen des unreinen Methanolstroms in eine Zwischensektion einer extraktiven Destillationszone;
(b) Einführen eines extraktiven Solvensstroms bestehend aus einer aus der Gruppe bestehend aus Wasser, Glycolen, Glycolethern und deren Mischungen ausgewählten Polarsubstanz in eine Obersektion der extraktiven Destillationszone;
(c) Destillieren Acetaldehyd am Kopf von der extraktiven Destillationszone; und
(d) Wiedergewinnen eines Bodenstroms von einer Untersektion der extraktiven Destillationszone, umfassend Methanol und die Polarsubstanz und mit einer verminderten Acetaldehydkonzentration im Vergleich zu dem unreinen Methanolstrom.
- 20

2. Verfahren nach Anspruch 1, wobei die Menge des in der extraktiven Destillationszone eingeführten extraktiven Solvensstroms zumindest 25 Gewichtsprozent des unreinen Methanolstroms beträgt.

- 25 3. Verfahren nach Anspruch 1, wobei die Polarsubstanz aus der Gruppe bestehend aus Wasser, Propylenglycol und deren Mischungen ausgewählt wird.

4. Verfahren nach Anspruch 1, umfassend die zusätzlichen Schritte von Einführen des Bodenstroms in eine Zwischensektion einer fraktionierten Destillationszone, Destillieren von Methanol am Kopf von der fraktionierten Destillationszone, und Wiedergewinnen eines zweiten Bodenstroms umfassend die Polarsubstanz von einer Untersektion der fraktionierten Destillationszone.
- 30

5. Verfahren nach Anspruch 4, umfassend die zusätzlichen Schritte von Recyclen von zumindest einem Teil des zweiten Bodenstroms zu der extraktiven Destillationszone für Gebrauch als der extractive Solvensstrom.
- 35

6. Verfahren nach Anspruch 1, wobei zumindest 50% des Acetaldehyds in dem unreinen Methanolstrom am Kopf in Schritt (c) destilliert wird.

7. Verfahren nach Anspruch 1, wobei Methanol zumindest 60 Gewichtsprozent des unreinen Methanolstroms umfaßt.
- 40

8. Verfahren zum Entfernen von Acetaldehyd von einem unreinen Methanolstrom nach Anspruch 1, wobei der Strom zumindest 60 Gewichtsprozent Methanol umfaßt; der extractive Solvensstrom zumindest 85 Gewichtsprozent einer aus der Gruppe bestehend aus Wasser, Propylenglycol und deren Mischungen ausgewählten Polarsubstanz umfaßt; die Menge des eingeführten extraktiven Solvensstroms zumindest 25 Gewichtsprozent des unreinen Methanolstroms beträgt und zumindest 50% des Acetaldehyds in dem unreinen Methanolstrom am Kopf von der extraktiven Destillationszone destilliert wird.
- 45

9. Verfahren nach Anspruch 8, wobei der unreine Methanolstrom aus einem Epoxidierungsprozeß wiedergewonnen wird, wobei Propylen mit Hydrogenperoxid zur Rekation gebracht wird, unter Verwendung eines Titan enthaltenden Zeoliths als Katalysator und Methanol als ein Solvens.
- 50

10. Verfahren nach Anspruch 8, wobei der unreine Methanolstrom aus 60-80 Gewichtsprozent Methanol, 0,01-0,1 Gewichtsprozent Acetaldehyd and 5-40 Gewichtsprozent Wasser besteht.

- 55 11. Verfahren nach Anspruch 8, wobei die Menge des extraktiven Solvensstroms 40 bis 60 Gewichtsprozent des unreinen Methanolstroms beträgt.

12. Verfahren zum Entfernen von Acetaldehyd von einem unreinen Methanolstrom nach Anspruch 1, umfassend

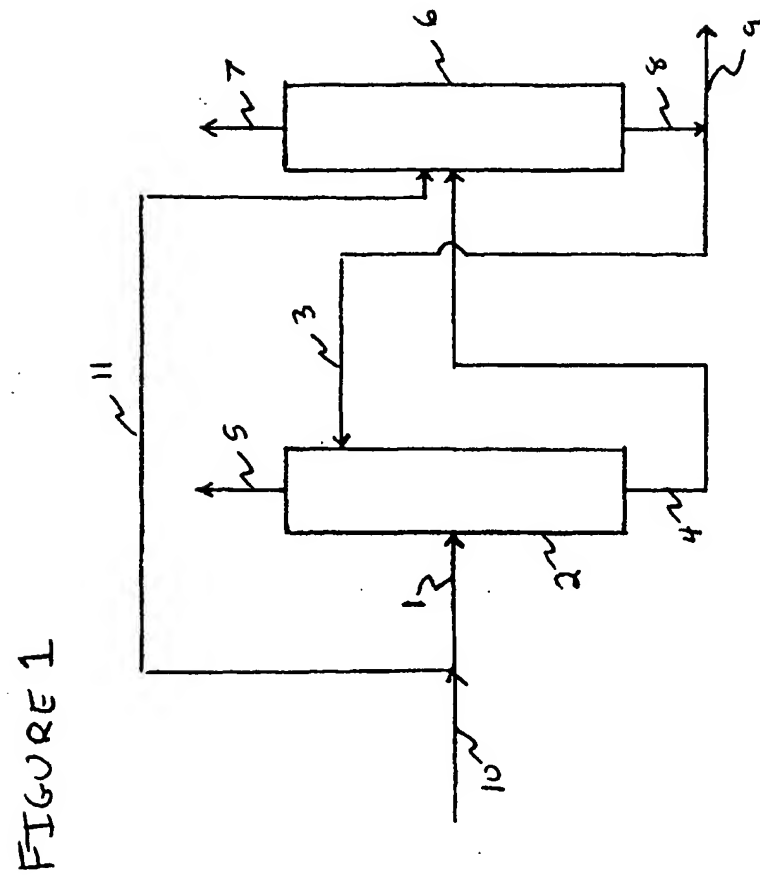
- (a) Einführen eines ersten Teils des unreinen Methanolstroms in eine Zwischensektion einer extraktiven Destillationszone; und darauf
- (e) Einführen des ersten Bodenstroms und eines zweiten Teils des unreinen Methanolstroms in eine Zwischensektion einer fraktionierten Destillationszone;
- (f) Destillieren eines gereinigten Methanolstroms am Kopf von der fraktionierten Destillationszone; und
- (g) Wiedergewinnen eines zweiten Bodenstroms von einer Untersektion der fraktionierten Destillationszone, bestehend aus der Polarsubstanz und mit einer verminderten Methanolkonzentration im Vergleich zu dem ersten Bodenstrom.
13. Verfahren nach Anspruch 12, wobei zumindest ein Teil des zweiten Bodenstroms für Gebrauch als der extraktive Solvensstrom in Schritt (b) recycled wird.
14. Verfahren nach Anspruch 12, wobei die Menge des in die extraktive Destillationszone eingeführten extraktiven Solvensstroms zumindest 25 Gewichtsprozent des ersten Teils des unreinen Methanolstroms beträgt.
15. Verfahren nach Anspruch 12, wobei der erste Teil des unreinen Methanolstroms 5 bis 30 Gewichtsprozent des unreinen Methanolstroms beträgt.
16. Verfahren nach Anspruch 12, wobei das Methanol zumindest 60 Gewichtsprozent des unreinen Methanolstroms umfaßt.
17. Verfahren nach Anspruch 12, wobei die Polarsubstanz aus der Gruppe bestehend aus Wasser, Propylenglycol und deren Mischungen ausgewählt wird.
18. Verfahren nach Anspruch 12, wobei zumindest 50% des Acetaldehyds in dem ersten Teil des unreinen Methanolstroms am Kopf in Schritt (c) destilliert wird.
19. Verfahren nach Anspruch 12, wobei der unreine Methanolstrom zusätzlich aus Wasser besteht, der extraktive Solvensstrom aus zumindest einer Polarsubstanz anders als Wasser besteht, und der zweite Bodenstrom einer zusätzlichen fraktionierten Destillation unterworfen wird zum Entfernen von Wasser am Kopf und zum Erhalten eines dritten Bodenstroms, bestehend aus der Polarsubstanz, die für Gebrauch als der extraktive Solvensstrom in Schritt (c) recycled wird.
20. Verfahren nach Anspruch 12, wobei die Polarsubstanz oder Mischung von Polarsubstanzen zumindest 85 Gewichtsprozent des extraktiven Solvensstroms umfaßt.

Revendications

1. Procédé pour extraire l'acétaldéhyde d'un flux de méthanol impur comprenant
- (a) l'introduction du flux de méthanol impur dans une section intermédiaire d'une zone de distillation extractive ;
- (b) l'introduction d'un flux d'un solvant extracteur constitué d'une substance polaire choisie dans le groupe des substances comprenant l'eau, les glycols, les éthers de glycol et les mélanges de ces substances dans une section haute de ladite zone de distillation extractive ;
- (c) la distillation de l'acétaldéhyde en tête de colonne de ladite zone de distillation extractive ; et
- (d) la récupération dans une section basse de ladite zone de distillation extractive d'un flux de résidus constitué de méthanol et de la substance polaire et possédant une concentration en acétaldéhyde réduite par rapport à celle du flux de méthanol impur.
2. Procédé selon la revendication 1, dans lequel la quantité de flux de solvant extracteur introduit dans ladite zone de distillation extractive est au moins de 25 pour cent en poids du flux de méthanol impur.
3. Procédé selon la revendication 1, dans lequel la substance polaire est choisie dans le groupe des substances comprenant l'eau, le propylène glycol et les mélanges de ces substances.
4. Procédé selon la revendication 1, comprenant les étapes supplémentaires d'introduction du flux de résidus dans une section intermédiaire d'une zone de distillation fractionnée, la distillation du méthanol en tête de colonne de

ladite zone de distillation fractionnée, et la récupération d'un deuxième flux de résidus composé de la substance polaire dans une section basse de ladite zone de distillation fractionnée.

- 5 5. Procédé selon la revendication 4, comprenant les étapes supplémentaires de recyclage d'au moins une portion du deuxième flux de résidus vers la zone de distillation extractive pour servir de flux de solvant extracteur.
6. Procédé selon la revendication 1, dans lequel au moins 50% de l'acétaldéhyde dans le flux de méthanol impur est distillé en tête de colonne selon l'étape (c).
- 10 7. Procédé selon la revendication 1, dans lequel le méthanol comprend au moins 60 pour cent en poids du flux de méthanol impur.
- 15 8. Procédé pour extraire l'acétaldéhyde d'un flux de méthanol impur selon la revendication 1, dans lequel le flux comprend au moins 60 pour cent en poids de méthanol ; le flux de solvant extracteur comprend au moins 85 pour cent en poids d'une substance polaire choisie dans le groupe des substances comprenant l'eau, le propylène glycol et les mélanges de ces substances ; la quantité de flux de solvant extracteur introduit est au moins de 25 pour cent en poids du flux de méthanol impur ; et au moins 50% de l'acétaldéhyde dans le flux de méthanol impur est distillé en tête de colonne de ladite zone de distillation extractive.
- 20 9. Procédé selon la revendication 8, dans lequel le flux de méthanol impur est récupéré par un processus d'époxidation dans lequel le propylène est amené à réagir avec du peroxyde d'hydrogène, une zéolithe contenant du titane est utilisée comme catalyseur et du méthanol comme solvant.
- 25 10. Procédé selon la revendication 8, dans lequel le flux de méthanol impur est composé de 60 à 80% en poids de méthanol, 0,01 à 0,1% en poids d'acétaldéhyde, et 5 à 40% en poids d'eau.
11. Procédé selon la revendication 8, dans lequel la quantité de flux de solvant extracteur est de 40 à 60 pour cent en poids du flux de méthanol impur.
- 30 12. Procédé pour extraire l'acétaldéhyde d'un flux de méthanol impur selon la revendication 1, comprenant
 - (a) l'introduction d'une première portion du flux de méthanol impur dans une section intermédiaire d'une zone de distillation extractive ; et suivie de
 - 35 (e) l'introduction du premier flux de résidus et d'une seconde portion du flux de méthanol impur dans une section intermédiaire d'une zone de distillation fractionnée ;
 - (f) la distillation d'un flux de méthanol purifié en tête de colonne de ladite zone de distillation fractionnée ; et
 - (g) la récupération dans une section basse de la zone de distillation fractionnée d'un deuxième flux de résidus composé de la substance polaire et possédant une concentration en méthanol réduite par rapport à celle du premier flux de résidus.
- 40 13. Procédé selon la revendication 12, dans lequel au moins une portion du deuxième flux de résidus est recyclée pour servir de flux de solvant extracteur selon l'étape (b).
- 45 14. Procédé selon la revendication 12, dans lequel la quantité de flux de solvant extracteur introduit dans ladite zone de distillation extractive est au moins de 25 pour cent en poids de la première portion du flux de méthanol impur.
15. Procédé selon la revendication 12, dans lequel la première portion du flux de méthanol impur est de 5 à 30 pour cent en poids du flux de méthanol impur.
- 50 16. Procédé selon la revendication 12, dans lequel le méthanol est composé d'au moins 60 pour cent en poids du flux de méthanol impur.
17. Procédé selon la revendication 12, dans lequel la substance polaire est choisie dans le groupe des substances comprenant l'eau, le propylène glycol, et les mélanges de ces substances.
- 55 18. Procédé selon la revendication 12, dans lequel au moins 50% de l'acétaldéhyde dans la première portion du flux de méthanol impur est distillée en tête de colonne selon l'étape (c).



EP 1 003 701 B1

19. Procédé selon la revendication 12, dans lequel le flux de méthanol impur est en outre composé d'eau, le flux de solvant extracteur est composé d'au moins une substance polaire autre que l'eau, et le deuxième flux de résidus est soumis à une distillation fractionnée supplémentaire afin d'extraire l'eau en tête de colonne et obtenir un troisième flux de résidus composé de la substance polaire qui est recyclée pour servir de flux de solvant extracteur selon l'étape (c).

20. Procédé selon la revendication 12, dans lequel la substance polaire ou le mélange de substances polaires comprend au moins 85 pour cent en poids du flux de solvant extracteur.